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SYSTEMATICS OF METAL–INSULATOR INTERFACIAL ENERGIES: A NEW RULE FOR WETTING AND STRONG CATALYST–SUPPORT INTERACTIONS

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This work concerns three questions: How can one decide whether a particular liquid metal will wet a given oxide substrate? What does analysis of experimental data tell one about the nature of the metal–substrate interactions? Is there correlation with strong metal–support intereactions in catalysis? Comparison of the trends predicted by the continuum results of Barrera and Duke with those observed shows that the dispersion contribution to metal–oxide interfacial energies cannot be the only important term. From the observed trends for non-reactive metal–oxide systems one deduces: (i) Wetting should be favoured by a low metal plasma frequency (i.e., low electron density). (ii) Wetting should be favoured by a small insulator bandgap. (iii) The insulator refractive index is especially useful as a classifier. It appears to be a rule that only for substrates with $n^2 \gtrsim 4.5$–5 does one find wetting by most non-reactive metals. The same rule is found for strong metal–support interaction, which should therefore correlate with wetting. (iv) Trace impurity effects are very pronounced whenever the impurity can react with the insulating substrate. Both the classification and the recognition of trace impurity effects have potential consequences in many applied problems, including substrate effects in support catalysts, liquid phase sintering and liquid metal embrittlement.

1. Introduction

This paper concerns phenomena at metal–oxide interfaces. The main emphasis is on the conditions under which liquid metals wet the oxide substrate. A secondary, related issue, draws parallels between systems which show wetting and supported-metal catalysts for which the catalytic metal–support interaction is strong. Finally, an empirical rule will be given classifying behaviour when the metal and oxide do not react chemically. It is found that the substrate refractive index is a useful classifying parameter.

Metal/non-metal interfaces are important in many physical phenomena. Some examples occur in technological applications: supported catelysts, brazing fluxes, protective coatings, and the many phenomena in which metal oxidation is central. Contacts between metals and semiconductors, together with the many situations in which metal colloids grow in non-metallic crystals

or glasses, are further examples. In a number of these cases the interfacial energy is critical, since it influences both the precise interfacial morphology and the potential strength of the bonding (though one must emphasise that the effective physical strength may be determined by other factors than the ideal interfacial energy).

In practice, most observations of metal/non-metal bonding are of the *wetting angle* and of the *work of adhesion.* These can be related to a number of separate interfacial energy components. Since there is room for semantic confusion, the term "surface tension" will not be used here. The quantity which is important is the surface energy (equal to the traditional surface tension only for a liquid) and not the surface stress (see Stoneham [1] for further discussion of this point). Suppose the several interfacial energies involving the three phases normally present are written σ_{ab} (with a, b given by i = insulator, m = metal, g = vacuum or other gas phase). Then two of the most important measurable quantities are these:

$$\text{Wetting angle } \theta: \qquad \cos\theta = (\sigma_{ig} - \sigma_{im})/\sigma_{mg}, \tag{1}$$

$$\text{Work of adhesion } w_a: \qquad w_a = \sigma_{mg} + \sigma_{ig} - \sigma_{im}, \tag{2}$$

where, to be specific, we consider a metal droplet (if liquid) on an insulating substrate. The recent survey by Naidich [2] contains a comprehensive list of data for wetting angles and work of adhesion. Since there is no reason why σ_{mg} should not be less than $\sigma_{ig} - \sigma_{im}$, the magnitude of the right-hand side of (1) may exceed unity, i.e. θ would be complex. When this happens, one finds spreading for positive values; for negative values, contact is only maintained by external forces.

For present purposes, the important feature is that $\cos\theta$ allows an immediate qualitative comparison of σ_{ig} and σ_{im}. Irrespective of many fine details (for there are manifest inconsistencies among the measurements, including differences from one worker to another), one can be relatively confident of the sign of $\cos\theta$, and hence of which is the larger of these two energies. Likewise, the broad order of magnitude of the work of adhesion can be obtained even when the division into the several components of eq. (2) remains uncertain. These features are exploited in the next section to give information about mechanisms of binding and the relative importance of different factors. The "mapping" of wetting/non-wetting behaviour against materials parameters chosen from simple models allows one to analyse the behaviour empirically and to identify rules of practical value.

2. Interfacial energies

2.1. General

There are many contributions to metal–ionic interaction energies, some large, some small, and others involving cancellations of terms. It will become clear that most depend on (or at least vary systematically with) the same small group of parameters, namely band gaps and plasma frequencies. It is convenient to divide these contributions into those which depend on the precise epitaxial relationship of metal and insulator and those which do not (A.M. Stoneham and P.W. Tasker, unpublished work, 1979; see also ref. [1]). Those which are principally independent of epitaxy include all those for which the metal can be regarded as a jellium. These are the image terms (i.e., the interactions of ions in the ionic phase with their image charges in the metal), the effects of conduction electron spillover into the ionic on the metal surface energy, the modifications of the interactions in the outer layers of the ceramic by this spillover, and the major part of the dispersion (Van der Waals) term. Those which do involve epitaxy include a part of the dispersion term, the short-range repulsive interactions, and the modification of the conduction-electron–core interaction in the metal because of the changes in the conduction electron density which are induced by the external ionic potential (this last contribution has been analysed by Gubanov and Dunaevski [3]). If a strict epitaxial relation of metal to ionic is observed, the epitaxy-dependent terms need only be a small fraction (above kT per atom at the equilibrium temperature) of the total interfacial energy (frequently of order 1 eV/atom).

All these components refer to an ideal system, and ignore important factors associated with surface roughness, chemical reaction, and impurity effects. In many cases it is easy to identify the likely exothermic reactions and the products, which are often complex oxides. In some cases the reactions are less obvious: Al on Al_2O_3 is an example, where there is often sufficient oxygen to make the system behave as if metal and oxide react. The volume of Pask and Evans [4] includes several discussions of different types of reactive system. It is important to add too that some ceramic surfaces may be stabilised only in the presence of metal. Tasker [5] has shown that certain types of free surface have infinite surface energy. However, the interfacial energy of such a surface with a metal may be finite, for certain of the long-range fields can be screened out.

2.2. Dispersion contributions

It is widely believed that the major contributions to "ideal" interfacial energies comes from dispersion forces. This assumption has been the basis of many rough estimates and, whilst there may be very good reasons for doubting the calculations in detail, there is no doubt that some of the trends and broad

magnitudes are satisfactory (see Naidich [2], Benjamin and Weaver [6], and Rossington and Harding [7]). Whilst even better-founded calculations verify that dispersion terms could dominate, it remains obscure why other terms cancel, and the extent to which these other terms do so systematically.

Most published calculations (e.g., ref. [2] or the more advanced approaches of ref. [8]) regard the surface as an ensemble of atoms interacting by pairwise terms; often further, possibly gross, simplications are added. In looking for systematic trends it is helpful to go to the opposite extreme, and to exploit the continuum results of Barrera and Duke [9,10]. Any continuum result contains its own simplifications, e.g. that there is no dependence on the precise crystal planes in contact. However, the important feature of Barrera and Duke's approach is that the interfacial energy for each of the interfaces (vacuum/metal, vacuum/non-metal and metal/non-metal) are defined by the frequency-dependent dielectric constants. Analytic, though very complicated, expressions are given in ref. [9]. If one assumes that plasmon damping is negligible in both metal and non-metal (the figures of ref. [9] suggest this is not a critical assumption) then, after complex algebra, an important and simple result emerges. Wetting ($\theta < \pi/2$) will occur only when the metal plasma frequency ω_{pm} is less than a critical value ω_{pm}^{c} given by:

$$\omega_{pm}^{c} = 2\sqrt{2}\left[\left(\omega_{pi}^{2} + 2\Delta^{2}\right)^{1/2} - 2\Delta\right] \tag{3}$$

Here Δ is the non-metal band gap, and ω_{pi} the non-metal plasma frequency. Whilst this result is not given by Barrera and Duke, it is verified by some of the numerical results in their figures. A fuller discussion and related extensions of (3) are given in ref. [10].

Expression (3) has several important aspects. Wetting is favoured by those systems for which (in units of the non-metal plasma frequency ω_{pi}) neither the gap Δ nor the metal plasma frequency are too large. Further, if Δ exceeds $\omega_{pi}/\sqrt{2}$, wetting is not possible. In section 3 the observed and predicted trends will be compared. This allows a further check of the continuum dispersion model, and it also leads to a classification of the behaviour of interfaces between non-metals and (non-reactive) metals.

3. Analysis of available data

Expression (3) involves three parameters: plasma frequencies for metal and non-metal, and the non-metal band gap. In all cases observed values are used (i.e., the predictions from jellium models for ω_{pm} are not used), though gaps in the data available limit the systems which can be analysed.

We have used the bulk plasmon values for the metal [11] in all cases. These show systematic features. The metals divide themselves into three main groups.

First there are noble metals like Ag and Au, together with some transition metals (e.g. Cr) with high plasma frequencies around 25 eV. At the opposite extreme are the strongly electropositive alkali metals and most alkaline earths, with values less than 10 eV. In between, one has the most of 3d transition metals, Pb, Sn, Al and many other cases.

The non-metals have plasmon energies in the range 10–30 eV as a rule; they are all greater than the bandgap in the cases observed. The trends in $\Delta/\hbar\omega_{pi}$ are more systematic; indeed, one can see from the form of dielectric function used by Barrera and Duke that there is a strong correlation with electronic polarisation. If one assumes their $\epsilon(0)$ is essentially the usual ϵ_∞, one has

$$\Delta/\hbar\omega_{pi} \sim (\epsilon_\infty - 1)^{-1/2}. \tag{4}$$

The observed values of Δ and $\hbar\omega_{pi}$ show the alkali halides have values of the ratio $\Delta/\hbar\omega_{pi}$ in a narrow range 0.5 to 0.6. For "ionic" oxides, excluding CdO, values are typically 0.3–0.5. As one progresses from diamond to Si and Ge, $\Delta/\hbar\omega_{pi}$ falls, as expected from the above relation to ϵ_∞.

Since there are gaps in available data, we shall use values of $\Delta/\hbar\omega_{pi}$ both from separate measurements of Δ and $\hbar\omega_{pi}$ and from eq. (4). There are modest but significant differences between the two values, which can be seen from fig. 1. For this reason we have assembled "wetting/non-wetting maps" for the various systems on two separate diagrams. Fig. 2a uses experimental values of

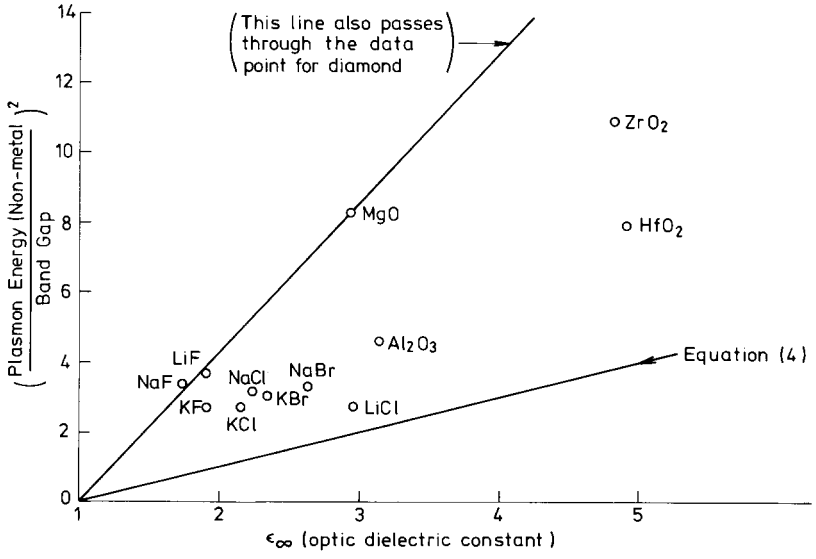

Fig. 1. Observed correlation between ϵ_∞ and Δ and $\hbar\omega_{pi}$. The lower line corresponds to eq. (4); the upper line also passes through the data points for diamond.

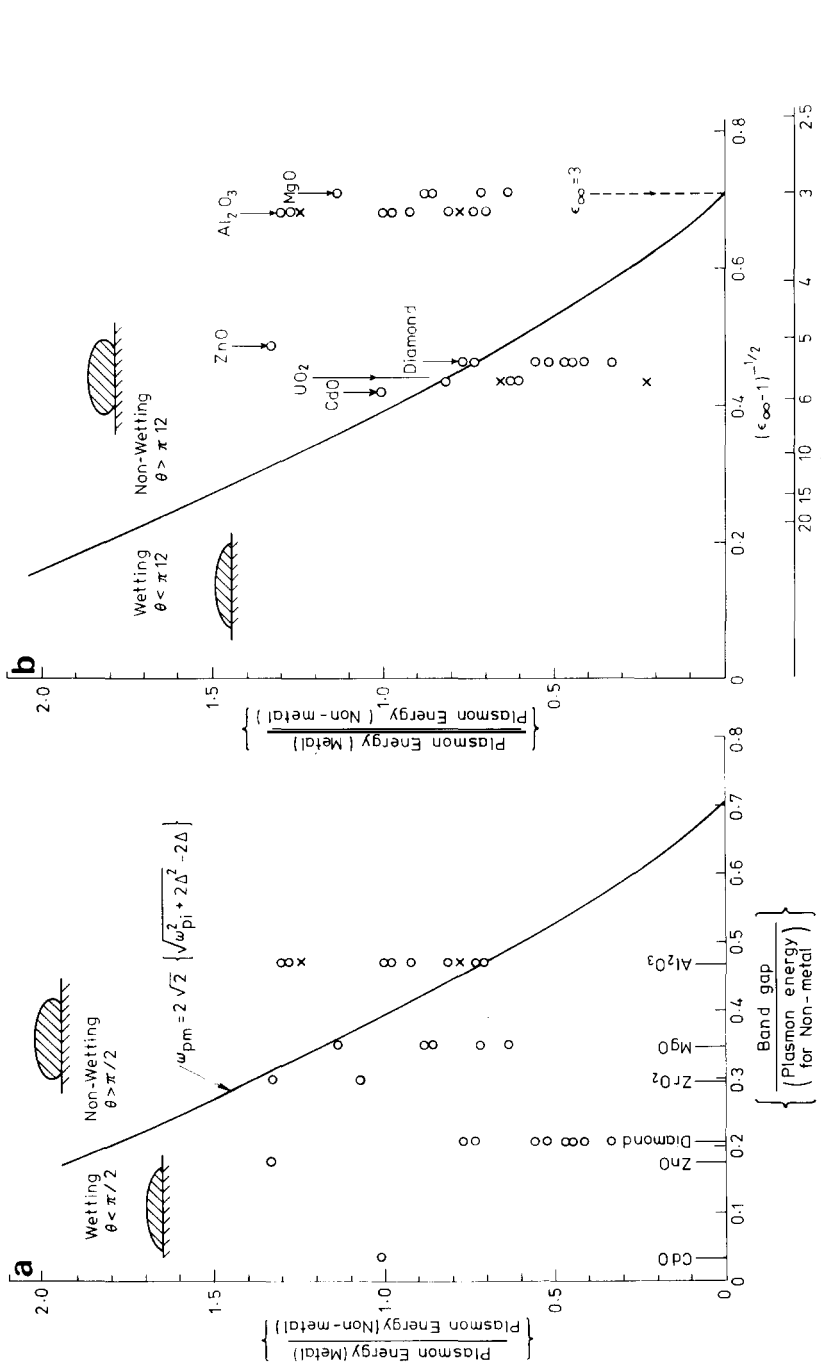

Fig. 2. For which systems should $\cos\theta$ have a given sign? The dividing curve is obtained from Barrera and Duke's equation (43a), subject to the assumption of zero plasmon damping and equal cutoff wavevectors for both condensed phases. (a) Data shown where the abscissa uses the experimental values of the bulk plasmon energy and band gap. (b) Data rearranged using eq. (4) for the abscissa $\Delta/\hbar\omega_{pl}$. Cases where $\theta < \pi/2$ (wetting) are given as circles; those with $\theta > \pi/2$ (non-wetting) are given as crosses.

$\hbar\omega_{pi}$ and Δ; fig. 2b uses $(\epsilon_\infty - 1)^{-1/2}$ instead of $\hbar\omega_{pi}/\Delta$; in both cases the observed plasmon energies are used in $\hbar\omega_{pm}/\hbar\omega_{pi}$. These two maps test how well the continuum model characterises interfacial energies.

We may now look for systematic trends with both metal and insulating substrate. There are three main tests. The first relates to dependence on the metal. Specifically, on a given substrate, $\cos\theta$ should vary systematically with metal plasma frequency; alternatively (and more generally) if the metals are ordered according to their value of θ, the same sequence should be found for several substrates. Naidich's data allow only a limited check for the species within specific subgroups (Au, Ag), (Ni, Cu, Co, Fe), (Sn, Pb, Ga, In) on MgO, Al_2O_3, SiC, diamond and (though strictly a different case) graphite. One finds systematic order maintained within each of the subgroups bracketed here (with some gaps where data are not given). However, there is only a rough correlation with plasmon energy (Cu and Ni always have θ larger than Co or Fe) and this correlation does not hold between these subgroups.

The second feature gives rather direct evidence that only a part of the interfacial energy is given by the dispersion contribution in the continuum form. In some cases there is an observed dependence of θ on the crystal face of the ionic substrate. This is especially dramatic for liquid Fe on MgO (e.g., Kingery et al. [12], p. 210) where $\theta < \pi/2$ for the (100) face of single-crystal MgO, $\theta = \pi/2$ on the (111) face, and $\theta > \pi/2$ for the (110) face. No dependence on face is expected in the continuum theory. That observed for Fe on MgO is, in fact, consistent with most of the face dependence coming from the insulator–vacuum surface energy (see, e.g., Tasker [13]).

The third test, that of classification into wetting/non-wetting cases, is most conveniently considered in a later section.

4. Expected trends in other contributions

Since the pure dispersion terms give only partial success, it is worth commenting on the other contributions to the various energies. In assessing how well the classification succeeds, one should not lose sight of the considerable experimental difficulties, notably from contaminated surfaces, nor of the inconsistencies in reported data.

Repulsive interactions. These short-range interactions should depend on the extent to which the atomic core in the metal fills the Wigner–Seitz sphere. One expects them to be less important for alkali metals and "free electron" systems.

Spillover effects. The charge transferred from metal to insulator (presumably mainly to the insulator cations) increases for metals of low work function. The work function W, like the plasmon energy, has systematic trends (Michaelson [14]):

Low W ($\lesssim 3$ eV): alkali metals, some alkaline earths.

Intermediate W: many metals, including 3d transition elements.
High W ($\gtrsim 5$ eV): noble metals Au, Pt, Ir, Pd, and some non-metals (As, Se).

Low work functions should imply a large spillover contribution, presumably lowering σ_{im} relative to σ_{ig}, and making wetting more likely (though, if θ is not near $\pi/2$, θ may be altered either way because of changes in σ_{mg}).

Chemical reaction terms. These are possibly the key to most of the problems. Naidich comments on many cases where reactive metals are observed to wet ($\theta \sim 0$). Indeed, the addition of perhaps 1% of a reactive metal may be enough to ensure wetting. Such cases we may call "intrinsic" reaction contributions. Just because modest concentrations are so effective, we should also anticipate that chemical impurities (O, S, C, H and N) may also be effective at very low levels. Impurity effects on σ_{mg} are well known, including strong effects of S and O on liquid Fe (e.g., Kingery et al. [12], pp. 207 and 215, and Halden and Kingery [15]. Likewise, there is a large literature on trace impurity effects on grain boundary energies, where there are parallel features.

5. Wetting or non-wetting?

Figs. 2a and 2b show the extent to which the criterion based on the Barrera–Duke theory actually classifies available data. We note the following features:

(1) The classification using the observed band gap and insulator plasmon energy is very poor.

(2) The classification based on ϵ_∞, whilst still limited, is much more successful. Indeed, it can be improved by changing the critical value of ϵ_∞ (at which the wetting/non-wetting boundary corresponds to $\omega_{pm} = 0$) from $\epsilon_\infty^c = 3$ (obtained from eqs. (3) and (4)) to a larger value. If the diamond data are genuinely free from chemical reaction terms one needs $\epsilon_\infty^c \sim 5.9$; if, however, the diamond data are subject to trace impurity or chemical effects, then ϵ_∞^c in the range 4–5 would seem optimal.

There is a rule therefore that *non-reactive liquid metals wet substrates with a high refractive index* ($\epsilon \gtrsim 4.5$ to 5, $n \gtrsim 2.1$ to 2.2). This is apparent partly from the data in fig. 2, but also from the many other cases (e.g. table 1) where the full details needed for the figure were not all available. In all cases of exceptions some sort of ad hoc explanation could be devised, but this is probably not too useful. In particular, several exceptional cases are close to the dividing line, e.g. UO_2 and CdO.

Table 1
Classification of metal/oxide systems

Substrate ϵ_∞	Do non-reactive liquid metals wet the oxide substrate?	Is there strong catalyst–support interaction?	
		(a) For In	(b) For Pt
< 3	SiO_2, BeO [a], MgO, Al_2O_3 [a],	MgO, SiO_2, Al_2O_3	SiO_2, Al_2O_3
3–4	CaO	Sc_2O_3, Y_2O_3	
4–5	ZrO_2, ThO_2, ZnO	HfO_2, ZrO_2	
Non-wetting		No metal–support interaction	
Wetting		Strong metal–support interaction	
5–6	$NiO(UO_2)$ [b], Cr_2O_3 [b], CdO [b]	Ta_2O_5	
		Nb_2O_5	
> 6	TiO_2, Fe_3O_4 [c]	TiO_2	TiO_2
		V_2O_3 (metallic)	

[a] Most cases do not wet. Wetting is claimed in some individual cases.

[b] These systems are close to the boundary; in Cr_2O_3 only data for Fe are available; for CdO only Ag data are available, and this case does not appear to wet.

[c] The dielectric constant does not appear to be given in the literature. However, ϵ_∞ is clearly greater than 6 for both FeO and Fe_2O_3. The other values of ϵ_∞ used are Al_2O_3 (2.9), BeO (2.49), CaO (3.28), CdO (5.4–6.2), Cr_2O_3 (5.7–6), HfO_2 (4.9), MgO (2.95), Nb_2O_5 (5.4), NiO (5.7–6.1), SiO_2 (2.4), Ta_2O_5 (4.6), ThO_2 (4.63), TiO_2 (6.8–8.4), UO_2 (5.3), ZnO (4.1), ZrO_2 (4.75).

6. Supported metal catalysts

The classification of behaviour according to ϵ_∞ has some further support from catalyst work reviewed recently by Moss [16] and by Tauster et al. [17]. First, Tauster and Fung [18] have looked at Ir on eleven oxide substrates. They find strong metal–support interaction in four cases (the last Ta_2O_5, being less active):

TiO_2 ($\epsilon_\infty = 6.8$ to 8.4), V_2O_3 (metal), Nb_2O_6 (5.4), Ta_2O_5 (4.6).

In seven cases there was no such metal–support interaction:

HfO_2 ($\epsilon_\infty = 4.9$), ZrO_2 (4.75), Al_2O_3 (2.9), MgO (2.95),

SiO_2 (2.4), Sc_2O_3 (?), Y_2O_3 (?)

Clearly there is quite a reasonable division between those with $\epsilon_\infty \gtrsim 5$, which show strong interactions, and those with $\epsilon_\infty \lesssim 4.5$, which do not. The authors suggest it is the reducibility of the oxide which is critical. This may be so; we

note, however, that the division corresponds very closely with that discussed in section 5. Some further support comes from observations of Pt on several substrates, where again the different behaviour of TiO_2 from Al_2O_3 and SiO_2 (Baker et al. [19]) is in accord with the classification by ϵ_∞. It would be naive to expect ϵ_∞ to classify correctly all cases. However, it is worth adding that other summaries of data (e.g. Tauster et al. [20]) fit too, the possible exceptions being those of borderline ϵ_∞ (ThO_2, ZrO_2, HfO_2) and the range of behaviour reported for TiO_2.

At this stage it is useful to look again at the wetting/non-wetting boundary as given by a classification according to ϵ_∞. We can include now those insulators for which data were too incomplete to be given in figs. 2a and 2b. The results, shown in table 1 show a strong (if incomplete) division consistent with the view wetting needs $\epsilon_\infty \gtrsim 5.3$. The refractive index ($\epsilon_\infty^{1/2}$) gives a useful guide to both wetting and catalytic behaviour. To a first approximation there is a rule that *systems which give strong metal–support interaction in catalysis should be those where the liquid metal wets the substrate.* The large body of data (which includes borides, carbides and nitrides as well as oxides (Samsonov and Vinitskii [21]) on wetting can be used to identify whether metal–support interactions are likely to be important.

7. Conclusion

A systematic survey of available data for wetting angles of non-reactive liquid metals on non-metals leads to two important conclusions. First, dispersion forces do not classify systems correctly as wetting or non-wetting, at least in simple models. Secondly, the non-metal refractive index provides a simple classifying rule, namely higher refractive indices than a critical value lead to wetting. Further comparison shows that it is just these systems which exhibit strong metal–support interactions in catalysis. Whilst these rules are empirical, there seems little doubt that the trends in refractive index are paralleling trends in the various factors directly involved in the metal/non-metal interactions.

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